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(54) Process for preparation of polyol fatty acid ester and glyceride mixture obtained.

(57) A polyol fatty acid ester having mixted acid groups is produced by reacting a partial ester of a polyol and a branched fatty acid with a a straight fatty acid or a lower alcohol ester thereof in the presence of a lipase. The obtained glyceride mixture contains a large amount of diglyceride having a branched, saturated fatty acid group and a straight, saturated fatty acid group.

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(54) Process for preparation of polyol fatty acid ester and glyceride mixture obtained.

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Process for Preparation of Polyol Fatty Acid Ester and Glyceride Mixture obtained

The present invention relates to a process for the preparation of polyol fatty acid esters. More particularly, the present invention relates to a process for preparing a polyol fatty acid ester having a mixed acid residue of a branched fatty acid and a straight chain fatty acid in the molecule at a high purity easily obtained according to the enzyme method. Then the invention relates to a glyceride mixture obtained by the process and a composition containing the glyceride mixture for the external use and cosmetic use.

(Statement of Prior Arts)

As the process for the industrial production of fatty acid esters, which is practically worked, there can be mentioned an esterification process and an alcoholysis process. However, a process for preparing at a high purity a polyol fatty acid ester having a mixed acid residue of a branched fatty acid and a straight-chain fatty acid in the molecule, which is intended in the present invention, is much restricted.

In the case where a polyol is esterified with a mixed fatty acid of a branched fatty acid and a straight-chain fatty acid in the presence or absence of a catalyst, since the reactivity of hydroxyl groups of the polyol is not selective, various polyol fatty acid esters having random ester linkages are synthesized.

For example, in the synthesis of a glycerol ester with a branched fatty acid (B) and a straight-chain fatty acid (S), if the triglyceride is intended, there is formed a mixture in which six triglycerides

$$\begin{bmatrix} B \\ B \\ B \end{bmatrix}, \begin{bmatrix} B \\ B \\ S \end{bmatrix}, \begin{bmatrix} B \\ S \\ B \end{bmatrix}, \begin{bmatrix} B \\ S \\ S \end{bmatrix}, \begin{bmatrix} S \\ B \\ S \end{bmatrix} \text{ and } \begin{bmatrix} S \\ S \\ S \end{bmatrix}$$

are radomly distributed according to the fatty acid composition, wherein $\left[\begin{matrix} \\ \\ \end{matrix}\right.$ represents glycerol. If the diglyceride is intended, there are formed three diglycerides

$$\begin{bmatrix} B \\ B \end{bmatrix}, \begin{bmatrix} B \\ S \end{bmatrix} \text{ and } \begin{bmatrix} S \\ S \end{bmatrix}$$

(neglecting the distinction between 1,2-diglyceride and 1,3-diglyceride) and the above-mentioned triglyceride mixture.

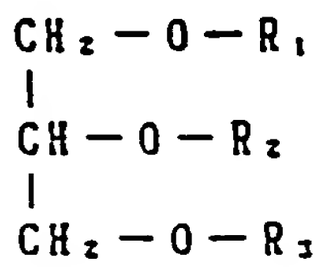
As the process for preparing a polyol ester having a mixed acid residue of a branched fatty acid and a straight-chain fatty acid (in the above-mentioned example,

$$\begin{bmatrix} B \\ B \\ S \end{bmatrix}, \begin{bmatrix} B \\ S \\ B \end{bmatrix}, \begin{bmatrix} B \\ S \\ S \end{bmatrix} \text{ or } \begin{bmatrix} S \\ B \\ S \end{bmatrix}$$

in the case of the triglycride and $\left[\begin{matrix} B \\ S \end{matrix}\right.$ in the case of the diglyceride), there can be considered a process in which a mixture formed by the esterification is subjected to the solvent fractionation and a fraction of the ester having a mixed acid residue is concentrated. However, if the difference of the melting point or solubility is small, the concentration is substantially impossible, and even if a high concentration is obtained, the yield is very low and the process is not practically satisfactory.

There can be considered another process in which a partial ester of a branched fatty acid or a straight-chain fatty acid is synthesized in advance by the esterification and the partial ester is reacted with a halide or the like of the remaining fatty acid (a straight-chain fatty acid for the partial ester of the branched fatty acid or a branched fatty acid for the partial ester of the straight-chain fatty acid). Also in this process, however, since the remaining hydroxyl group of the partial ester has no selectivity, a product esterified selectively at a predetermined position cannot be efficiently obtained. Moreover, a product satisfactory in the quality and safety can hardly be obtained.

The di-acylglycerol obtained in the invention is defined with the formula (I):



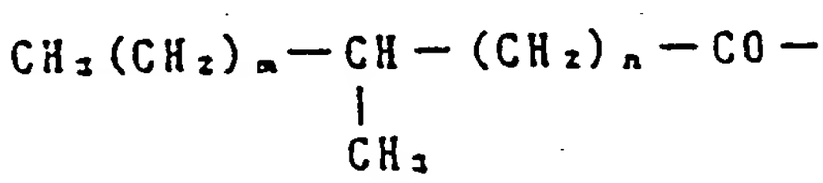
... (I)

in which one of R1, R2 and R3 is a straight-chain fatty acid residue, saturated or unsaturated, group having 8 to 22 carbon atoms, another is a branched, saturated fatty acid residue having 7 to 24 carbon atoms and the other is hydrogen.

It is preferable that one of R1, R2 and R3 is a straight-chain fatty acid group having 18 to 22 carbon atoms, another is 2-ethylhexanic acid group and the other is hydrogen.

It is also preferable that one of R1, R2 and R3 is a branched, saturated fatty acid group selected from the group consisting of:

(a) methyl-isostearic acid group having the formula:



in which m and n each are an integer of 4 to 10, the sum total of m and n is 14 and m and n each have a distribution with its center of 7,

(b) 5,7,7-trimethyl-2-(1,3,3-trimethylbutyl)octanoic acid group and

(c) 2-heptylundecanoic acid group, another is teteradecanoic acid group and the other is hydrogen.

The invention, in addition, provides a glyceride mixture which comprises zero to 40 percent by weight of monoglyceride, 60 to 100 percent by weight of diacylglycerol and zero to 20 percent by weight of triglyceride,
the acyl group of the glycerides being selected from (i) a straight-chain fatty acid residue having 8 to 22 carbon atoms and (ii) a branched, saturated fatty acid residue having 7 to 24 carbon atoms,
the diglyceride comprising 60 to 100 percent by weight of the di-acylglycerol having both groups (i) and (ii), zero to 40 percent by weight of the di-acylglycerol having two groups (i) and zero to 40 percent by weight of the di-acylglycerol having two groups (ii).

The invention provides an external preparation which comprises the glyceride mixture as defined above and a cosmetic component for the skin or hair or a medical drug, a cosmetic composition which comprises the glyceride mixture and a cosmetic component and an oily composition containing the glyceride mixture.

The present invention will now be described in detail.

As the polyol used in the present invention, there can be mentioned alkanediols such as ethylene glycol, propylene glycol (1,2-propanediol), 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 1,5-pentanediol, 2,4-pentanediol, 1,6-hexanediol, 2,5-hexanediol, 1,8-octanediol and 2,7-octanediol, alkanetriols such as 1,2,4-butanetriol, glycerol and 1,2,6-hexanetriol, and dimers, trimers and polymers thereof represented by diglycerol.

As the branched fatty acid and straight-chain fatty acid used in the present invention, there can be mentioned saturated and unsaturated fatty acids having 4 to 24 carbon atoms. As the branched fatty acid, there can be mentioned, for example, trialkylacetic acids, 2-alkyl-branched acids, methyl-branched acids and polybranched acids. More specifically, there can be mentioned 2-ethylhexanoic acid, isopelargonic acid, isomyristic acid and isostearic acid. As the straight-chain fatty acid, there can be mentioned valeric acid, caproic acid, enanthoic acid, caprylic acid, pelargonic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, behenic acid, lignoceric acid, palmitoleic acid, oleic acid, elaidic acid, erucic acid, sorbic acid and linoleic acid. These straight-chain fatty acids may be in the form of esters with a lower alcohol having 1 to 3 carbon atoms, such as methanol, ethanol or propanol. In the present invention, the above-mentioned branched fatty acids, straight-chain fatty acids and alcohol esters thereof can be used, but the fatty acids and lower alcohol esters are not particularly critical.

Any of lipases capable of synthesizing esters can be arbitrarily used for carrying out the present

Component \ Form of preparation (wt.%)	Ointment	Cream	Milky lotion	Lotion
oil	0 ∿ 70	0 ∿ 50	0 ∿ 20	0 ∿ 5.0
the diacylglycerin of the present invention	1 ∿ 50	0.5 ∿ 30	0.5 ∿ 10	0.1 ∿ 5.0
surfactant	0 ∿ 5.0	0.5 ∿ 5.0	0.5 ∿ 3.0	0.1 ∿ 2.0
polyhydric alcohol	0 ∿ 30	0 ∿ 20	0 ∿ 10	0 ∿ 40
water	0 ∿ 20	10 ∿ 70	30 ∿ 80	50 ∿ 90

The diacylglycerin represented by the general formula (I) to be used in the present invention is one which is liquid at room temperature, exhibits high resistance to oxidation and decomposition, is lowly irritant and imparts agreeable touch to skin or hair. Namely, although a diacylglycerin having residues of an unsaturated fatty acid such as oleic acid or a short-chain fatty acid such as octanoic acid is also liquid, a diacylglycerin having residues only of an unsaturated fatty acid is problematic in resistance to oxidation, while one having residues only of a short-chain fatty acid is problematic in irritativeness. In contrast to these diacylglycerins, the diacylglycerin of the present invention having, in its molecule, both a C_{18} branched fatty acid residue and a tetradecanoic acid residue is not problematic in these regards.

The external preparation containing the diacylglycerin as described above well fits skin owing to the absence of a crystalline substance therein and is excellent in the persistency of the humectant effect for skin.

Liquid oil

The prepared diacylglycerin having a branched saturated fatty acid residue and a myristic acid residue according to the present invention has the following characteristics: (1) it is liquid at ordinary temperatures, (2) it is chemically stable owing to its saturated hydrocarbyl group, (3) the decomposition of the myristoyl ester group is remarkably slight and (4) it is very agreeable to the touch of skin. Therefore, the diacylglycerin is useful particularly as a liquid oil for cosmetics or external preparations which are applied directly to the skin. A component which is crystalline at ordinary temperatures is inconvenient for handling, because it must be molten by heating prior to its use. Further, when such a component is contained in an emulsion system, it crystallizes with time to cause phase separation finally. The diacylglycerin having a branched saturated acid residue and a myristic acid residue according to the present invention is liquid at ordinary temperatures and exhibits, as a polar oil, a characteristic of stabilizing an emulsion system. The diacylglycerin according to the present invention may be used alone as a liquid oil for cosmetics or drugs or as a mixture with conventional oil, vaselin, liquid paraffin or natural fat.

Solid Cosmetic

The glyceride mixture thus obtained is decolored and deodorized by ordinary methods to give a colorless and odorless mixture mainly comprising the diglyceride of the present invention, which is not irritant to the skin and exhibits excellent amorphous properties including good spreadability. This mixture has excellent characteristics favorable for use as a solid oily base for cosmetics and drugs.

When the fatty acid diglyceride according to the present invention is prepared by a process as described above, it is generally obtained as a mixture of various glycerides. The content of the diglyceride represented by the general formula (I) in the mixture is at least 40% (by weight, the same applies hereinafter), preferably at least 50%. If the content is less than 40%, the glyceride mixture will be poor in spreadability and touch. Further, it is necessary that the content of a diglyceride having two residues of a

prepare isostearomristin diglyceride. In the obtained reaction product, the ester synthesis ratio was 90%. The ester synthesis ratio referred to herein is the ratio, expressed in terms of %, of the amount of the fatty acid consumed for esterification to the amount of the fatty acid as the substrate in the charged reaction mixture. The reaction product was passed through a thin-film evaporator at 190° C under 0.03 Torr to remove unreacted isostearin monoglyceride and myristic acid and obtain 1310 g of intended isostearomyristin diglyceride as the distillation residue.

The composition of the product was analyzed by gas chromatography (GLC) using a fused silica capillary (DB-1 supplied by J & W). It was found that the product comprised 3% of a monoglyceride, 89% of a diglyceride and 8% of a triglyceride and the diglyceride comprised 9% of diisostearin glyceride, 91% of isostearomyristin diglyceride and 0% of dimyristin glyceride.

Example 2

A four-neck flask having a capacity of 5 ℓ was charged with 1000 g (4.59 moles) of 2-ethylhexane monoglyveride, 1500 g (4.41 moles) of behenic acid and 200 g of a commercially available lipase preparation, Lipozyme 3A (lipase derived from Mucor miehei, immobilized on an anion-exchange resin; supplied by Novo Industri A.S.), and reaction was carried out at 75° C, under 220 Torr for 3 hours with stirring. The reaction product obtained at an ester synthesis ratio of 96% was passed through a thin-film evaporator at 185° C under 0.05 Torr to obtain 2210 g of 2-ethylhexanobehenin diglyceride as the distillation residue.

When the product was analyzed according to the GLC method described in Example 1, it was found that the product comprised 0% of a monoglyceride, 88% of a diglyceride and 12% of a triglyceride and the diglyceride comprised 0% of di-2-ethylhexane glyceride, 91% of 2-ethylhexanobehenin diglyceride or 2-ethylhexanoyl-behenoyl glycerol and 9% of dibehenoyl glycerol.

Example 3

A four-neck flash having a capacity of 5 ℓ was charged with 1000 g of a monoester of trimethylene glycol with isomyristic acide (3.50 moles; monoester synthesized by using isomyristic acid supplied by Nissan Kagaku), 1100 g (3.24 moels) of behenic acid and 200 g of Lipozyme 3A used in Example 2, and 2000 mℓ of hexane was further added to dissolve behenic acid. A tube for separating and refluxing hexane and water was set to the flask and reaction was carried out at 55° C with stirring under reduced pressure for 6 hours. The lipase preparation was removed by filtration. In the obtained reaction product, the ester synthesis ratio was 83%. In the same manner as described in the foregoing examples, the reaction product was passed through a thin-film evaporator at 200° C under 0.05 Torr to give 1730 g of an intended isomyristobehenic diester of triethylene glycol as the distillation residue.

By the GLC analysis of the obtained product, it was found that the product comprised 100% of a diester of trimethylene glycol and the diester comprised 2% of diisomyristic ester, 94% of isomyristobehenic ester or 1-isomyristoyl 3-behenoyl propanediol and 4% of dibehenate.

Example 4

A three-necked flask of 500 ml was charged with 92 g (1 mol) of glycerine and 144.2 g (1 mol) of 2-ethyl hexanate and then 0.5 g of potassium hydroxide and 1.0 g of activated carbon. This reaction mixture was heated up to 150° c to 260 ° c for 2 to 4 hours to effect esterification. The product mixture was found, by way of gas chromatography, to comprise 0.9% of the fatty acid, 24.6% of glycerine, 46.4% of monoglyceride, 23.2% of diglyceride and 5.0% of triglyceride. The analysis by the gas chromatography was conducted at an injection temperature of 350° c, determination temperature of 345° c, with a column of DB-1, at a column temperature of 100° c up to 340° c, at a flow rate of 10° c per minute.

The product mixture was neutralized with 85% phosphoric acid solution and it was heated at 150 to 240° c for 1 to 3 hours in nitrogen gas to top the unreacted glycerine and fatty acid. The activated carbon was removed out with filtration. Then molecular distillation was carried out to distil out the monoglyceride. The obtained composition was found to comprise a trace amount of the fatty acid, a trace amount of glycerine, 87.0% of monoglyceride, 13.0% of diglyceride and a trace amount of triglyceride.

Then another three-necked flask of 500 ml was charged with 73 g (0.281 mol) of the composition and

successively, with the generation of gas. During the dropwise addition, the reaction mixture was kept at a room temperature. After about 3 hours, the dropwise addition of thionyl chloride was completed. Then, the reaction mixture was kept at a temperature of 60 to 70 °C on an oil bath for about 3 hours. It was confirmed that the generation of gas nearly discontinued. The reaction mixture was distilled under a reduced pressure to remove low-boiling substances, followed by steam distillation. 588 g of a cut of 112 to 120 °C/0.1 to 0.3 mmHg was recovered (yield : 97 %). This cut was identified with 5,7,7-trimethyl-2-(1,3,3-trimethylbutyl)-octanoyl chloride.

IR spectrum (liquid film method)

2970, 2920, 2875, 1795 (C=O stretching), 1480, 1390, 1370, 1260, 1210, 995, 930, 790, 710, 600cm^{-1}

H^1-NMR spectrum (CCl_4 solvent) : δ

0.9 (s,24H,CH_3-)
1.1 ~ 2.0 (m,10H, -CH_2- and $-\overset{|}{\underset{|}{C}}-\underline{H}$)
2.5 (m,1H, $>C\underline{H}COCl$)

Referential Example 2

568 (2.0 mol) of isostearic acid (a methyl-branched fatty acid represented by the following formula; Emery 875 isostearic acid of Emery, U.S.A.) was reacted with 520 g (4.4 mol) of thionyl chloride in a 3-ℓ reactor fitted with the same devices as those used in Referential Example 1.

$$CH_3(CH_2)_m-\underset{\underset{CH_3}{|}}{CH}-(CH_2)_n-COOH$$

wherein m and n are each an integer of 4 to 10 with the proviso that the sum total of m and n is 14 and that both are distributed with a point of m = n = 7 as the center.

After the completion of the reaction, the reaction mixture was distilled under a reduced pressure to recover about 230 g of a low-boiling substance which was thought to be thionyl chloride. Then, the residue was further distilled under a reduced pressure to obtain 454 g of a cut of 153 to 170 °C/1.0 to 3.0 mmHg (yield : 75 %). This cut was identified with methyl-branched isostearoyl chloride.

IR spectrum (liquid film method)

2950, 2920, 2550, 1800 (C=O stretching), 1460, 1400, 1380, 950, 720, 680, 590cm^{-1}

H^1-NMR spectrum (CCl_4 solvent) : δ

$$0.6 \sim 1.0\ (m,\ C\underline{H}_3CH_2- \text{ and } -\underset{\underset{C\underline{H}_3}{|}}{CH}-)$$

1.0~1.5 (m, -$C\underline{H}_2$-)

this order into a 3-ℓ reactor fitted with a thermometer, a dropping funnel, a reflux condenser and a stirrer. The contents were heated to 50 °C on an oil bath under stirring, while passing nitrogen gas therethrough. 291 g (0.96 mol) of the 5,7,7-trimethyl-2-(1,3,3-trimethylbutyl)octanoyl chloride prepared in Referential Example 1 was dropwise added to the reactor through the dropping funnel over a period of about 3 hours, while keeping the reaciton mixture at about 50 °C. After the completion of the dropwise addition, the reaction mixture was heated to 60 to 80 °C and stirred for about 5 hours. The resulting mixture was filtered to remove a white precipitate of pyridine hydrochloride. The obtained filtrate was distilled in a vacuum to remove the solvent and heated to 190 to 200 °C under a reduced pressure of 0.5 to 0.7 mmHg for about 5 hours to remove the residual acyl chloride completely. The obtained product was a mixture comprising di- and triacylglycerins obtained by esterifying one molecule of monomyristoylglycerin with one or two molecules of 5,7,7-trimethyl-2-(1,3,3-trimethylbutyl)octanoic acid respectively and unreacted monomyristoyl-glycerin.

This mixture was subjected to column chromatography using Wako gel B-10 (mfd. by Wako Junyaku Kogyo) and a hexane/diethyl ether (70 : 30) mixture to obtain 360 g of a diacylglycerin fraction. This diacylglycerin fraction was a transparent and colorless liquid and identified with a diacylglycerin having a 5,7,7-trimethyl-2-(1,3,3-trimethylbutyl)octanoic acid residue and a myristic acid residue.

IR spectrum (liquid film method)

3500 (OH stretching), 2960, 2930, 2850, 1740 (C=O stretching), 1465, 1365, 1160, 720cm^{-1}

H^1-NMR spectrum (CCl_4 solvent) : δ

0.9 (s, 27H, -CH_3)
1.2 ~ 1.6 (m, 22H, -CH_2- and - C -H)
2.3 (m, 3H, - CH-CO-, CH_2-CO-)
2.9 (s, 1H, -OH)
4.0 ~ 4.5 (m, 4H, -CH_2-O-)
5.1 (m, 1H, >CH-OH)

Acid value : 0.1 (calculated : 0)
Hydroxyl number: 98.0 (calculated : 98.6)

Example 8

303 g (1 mol) of the monomyristoylglycerin prepared in Referential Example 4, 1500 ml of benzene and 100 g (1.27 mol) of pyridine were fed in this order into a 3-ℓ reactor fitted with the same devices as those used in Example 7. The contents were heated to 50 °C on an oil bath, while passing nitrogen gas therethrough. 291 g (0.96 mol) of the methyl-branched isostearoyl chloride prepared in Referential Example 2 was dropwise added to the reactor through the dropping funnel. After the completion of the dropwise addition, the contents were kept at 50 °C for about 3 hours and then at 70 to 80 °C for about 8 hours to thereby carry out the esterification completely. It was confirmed by IR spectroscopy that the reaction mixture did not contain any acyl chloride at all. The reaction mixture was treated in a similar manner to that used in Example 7 to obtain 372 g of a diacylglycerin having a methyl-branched isostearic acid residue and a myristic acid residue as a transparent and colorless liquid.

IR spectrum (liquid film method)

3480 (OH stretching), 2955, 2930, 2850, 1740 (C=O stretching), 1465, 1365, 1160, 720cm^{-1}

H^1-NMR spectrum (CCl_4 solvent) : δ

0.9 (m, 9H, -CH_3)

The obtained creams were subjected to the preservation test (state and odor) of 40°C and 3 months and monitor test. In the monitor test, each cream was applied to the faces of 86 women of 20 to 40 years old which had been sampled at random to evaluate the feeling thereof in service according to the criteria which will be described.

The results are shown in Table 1.

<Evaluation criteria>

A very moist and agreeable to the touch
B indefinably agreeable to the touch
C lacking in particular characters

Table 1

Example	Diacylglycerin	Preservation test 40°C/3 months	Monitor test		
			A	B	C
Example 7	5,7,7-trimethyl-2-(1,3,3-trimethylbutyl)octanoic acid/myristic acid	good	79	7	0
Example 8	methyl-branched isostearic acid/myristic acid	good	66	15	5
Example 9	2-heptylundecanoic acid/myristic acid	good	75	9	2

Composition Example 2 (Ointment)

<Oil phase components>	
vaseline	40 % by weight
squalane	10
diacylglycerin prepared in Example 8	20
POE(20) sorbitan monostearate	3
butylparaben	0.1
<Aqueous phase components>	
methylparaben	0.2% by weight
glycerin	10
water	the balance

An ointment was prepared from the above oil phase and aqueous phase components by the following process.

<Preparation process>

Methylparaben and glycerin were added to water and the obtained mixture was kept at 70°C. Separately, the other lipophilic components were molten by heating to obtain a molten mixture of 70°C. This mixture was added to the above aqueous phase component mixture, followed by emulsification with an emulsifier. The obtained emulsion was cooled to a final temperature of 30°C with a heat exchanger and charged to obtain an ointment according to the present invention.

The obtained ointment was an external preparation which exhibited high affinity for skin and was excellent in the persistency of the humectant effect for skin.

<Oil phase components>	
cetanol	1% by weight
squalane	5% by weight
olive oil	3
jojoba oil	2
diacylglycerin prepared in Example 9	5
POE(10) hardened castor oil	1
sorbitan monostearate	1
butylparaben	0.1
<Aqueous phase components>	
methylparaben	0.1% by weight
glycerin	2
1,3-butylene glycol	2
ethanol	3
perfume	0.1
water	the balance

A milky lotion was prepared from the above oil phase and aqueous phase components in a similar manner to the one described in Composition Example 3.

The obtained milky lotion was an external preparation which exhibited high affinity for skin and was excellent in the persistency of the humectant effect for skin.

Composition Example 5 (lotion)

<Oil phase components>	
diacylglycerin prepared in Example 8	2% by weight
POE(60) hardened castor oil	1% by weight
<Aqueous phase components>	
lactic acid	a suitable amount
sodium lactate	a suitable amount
glycerin	3% by weight
1,3-butylene glycol	1.5
polyethylene glycol 1500	0.5
ethanol	10
perfume	0.1
water	the balance

A lotion was prepared from the above oil phase and aqueous phase components by the following process.

<Preparation process>

Glycerin, 1,3-butylene glycol, polyethylene glycol 1500, lactic acid, sodium lactate and ethanol were dissolved in water to obtain a weakly acid aqueous solution (pH: 5 to 6). Separately, polyoxyethylene hardened castor oil, the diacylglycerin prepared in Example 5 and perfume were molten to obtain a molten mixture. This mixture was added to the above solution under stirring to obtain a lotion according to the present invention.

The obtained lotion was an external preparation which exhibited high affinity for skin and was excellent in the persistency of the humectant effect for skin.

Composition Example 6 (lip cream)

Table 2

	Fatty acid (a)	Fatty acid (b)	Glyceride composition[1]			Diglyceride composition[2]		
			mono-glyceride	di-glyceride	tri-glyceride	high-melting diglyceride	medium-melting diglyceride	low-melting diglyceride
Ex. 10	behenic acid	2-ethyl-hexanoic acid	0.5	99.0	0.5	2.9	94.1	2.0
Ex. 11	stearic acid	2-ethyl-hexanoic acid	<0.1	99.0	1.0	<0.1	94.7	4.3

Note) 1), 2): values (area ratios) as determined by gas chromatography

2): The "high-melting diglyceride" refers to a diester with a fatty acid (a) and the "low-melting diglyceride" refers to a diester with a fatty acid (b), while the "medium-melting diglyceride" refers to a mixed acid diester with fatty acids (a) and (b).

Table 4

Formulation / Evaluation item	Products of the present invention	
	A	B
Spreadability	ⓒ	○
Unclamminess to the touch	ⓒ	○
Unstickiness	ⓒ	○

In Table 4,

ⓒ: The number of women who reported that the lip cream was excellent in each item is 16 or above.
○: The number of women who reported that the lip cream was excellent in each item is 12 to 15.

It can be understood from the results shown in Table 4 that the lip cream according to the present invention is excellent in spreadability, unclamminess to the touch and unstikiness.

Further, it can be understood from the results shown in Fig. 1 that the lip cream according to the invention exhibits little temperature dependence of break strength and exhibits excellent feelings in service over a wide temperature range. when the break sgrength is lower than 200 g, the resulting lip cream will be too soft to retain its shape, while when it is higher than 600 g, the lip cream will be so hard as to be disagreeable to the touch.

Composition Example 7 (lipstick)

Lipsticks having compositions given in Table 5 were prepared and examined for performance by ten expert panellists.

The results are shown in Table 6.

Table 6

Evaluation item \ Sample code	Products of the present invention			
	I	J	K	L
Spreadability	○	◎	◎	◎
Unclamminess to the touch	○	○	◎	◎
Unstickiness	○	◎	◎	◎
Independence of spreadability and touch on temperature	○	○	◎	◎

(Note) Evaluation criteria

◎: At least eight out of the ten panellists rated the product good.

○: At least six out of the ten panellists rated the product good.

It can be understood from the above results that the lipstick according to the present invention is excellent in spreadability, unclamminess to the touch, unstickiness and independence of spreadability and touch on temperature.

Among the lip creams and lipsticks shown in Tables 3 and 5, the lip creams A and B and lipsticks J and K according to the present invention and the lip creams C and D and lipstick M for comparison were examined for sweating and blooming.

The sweating was evaluated by observing, with naked eyes, the sample which had been allowed to stand at 5 °C for 4 hours and then under the conditions of 35 °C and 60 RH for 4 hours, while the blooming was evaluated by observing, with naked eyes, the sample which had been allowed to stand at 35 °C for 8 hours and then at 5 °C for 24 hours.

Results are shown in Table 7, in which - indicates unobserved.

Table 7

Sample		Sample code	Sweating	Blooming
Lip cream	product of the present invention	A	-	-
		B	-	-
Lipstick	product of the present invention	J	-	-
		K	-	-

Neither sweating nor blooming was observed in the products of the present invention. It can be understood from this fact that the quality of the product of the present invention is very stable.

Table 9

Evaluation criteria \ Sample code	Product of the present invention	
	N	O
Drawing easiness	9	8
Softness	8	8
Smoothness	8	9

(Note) The figures in Table 9 each refer to the number of panellists who reported that the product was excellent as compared with the other.

point near the bodily temperature, the improvement is insufficient.

It can be understood from the results shown in Table 9 that a cosmetic of a pencil type which gives soft feeling and is excellent in smoothness can be obtained by using the diglyceride according to the present invention.

Composition Example 9 (compacted powder eye shadow)

Compacted powder eye shadows having compositions given in Table 10 were prepared by the method which will be described below and examined for physical properties and feelings in service.

The results are shown in Table 11.

<Preparation method>

The powder components were mixed in a blender by stirring to obtain a mixture. Separately, the oil components were homogeneously molten by heating and sprayed on the mixture, followed by stirring. The resulting mixture was pulverized and press molded in a molding machine to obtain a compacted powder eye shadow.

Note)

*1 Evaluation of impact resistance

Ten compacted powder eye shadows each placed in a dish-like case made of aluminum were made to fall from a height of 1 m on an iron plate to observe whether fracture, crack or cutout was present or not.

○: Neither fracture nor crack nor cutout was observed in any of the ten eye shadows.

*2 Evaluation of adherence to cosmetic chip

The surface of the eye shadow was rubbed with a cosmetic chip for eye shadow to determine the adherence of the eye shadow to the chip.

○: The eye shadow adhered uniformly.

*3. Evaluation of appearance, adherence to the skin and gradatability

The appearance, adherence to the skin and gradatability in service were evaluated by ten expert panellists.

○: 7 or more out of the ten panellists rated the product good.

It can be understood from the results shown in Table 11 that the product containing the diglyceride according to the present invention exhibits excellent performances including high impact resistance, good adherence to the skin and gloss-free appearance.

Composition Example 10 (eye shadow of cream type)

Eye shadows of a cream type having compositions given in Table 12 were prepared by the method which will be described below and examined for feelings in service by ten expert panellists.

The results are shown in Table 13.

<Preparation method>

Table 13

Evaluation item \ Sample code	Product of the present invention
	V
Spreadability	◎
Spreading lightness	◎
Stickiness	◎
Gradatability	◎

Claims

1. A process for preparing a polyol fatty acid ester having a mixed acid residues, which comprises the step of reacting a partial ester of a polyol and a branched fatty acid with a straight-chain fatty acid or a lower alcohol ester thereof in the presence of a lipase.

2. A process as claimed in Claim 1, in which the reaction is conducted while water is being removed out.

3. A process as claimed in Claim 1, in which the lipase is one to react with the polyol selectively at its alpha-position.

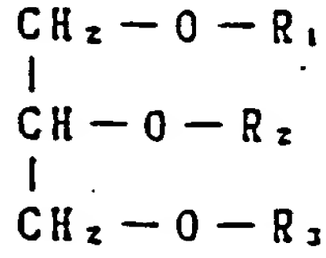
4. A process as claimed in Claim 1, in which said partial ester has a branched fatty acid residue being saturated and havihg 7 to 24 carbon atoms and said straight-chain fatty acid has 8 to 22 carbon atoms.

5. A glyceride mixture obtained by the process as defined in Claim 1 or 4.

6. A glyceride mixture obtained by the process as defined in Claim 1 or 4, which comprises 60 percent to 100 wt.%, of the di-acylglycerol having one branched acyl group and one straight-chain acyl group.

7. A glyceride mixture obtained by the process as defined in Claim 1 or 4, which comprises 60 to 97 wt.%, of the di-acylglycerol havihg one branched acyl residue and one straight-chain acyl residue.

8. A glyceride mixture obtained by the process as defined in Claim 1, in which the diglyceride has the formula (I):



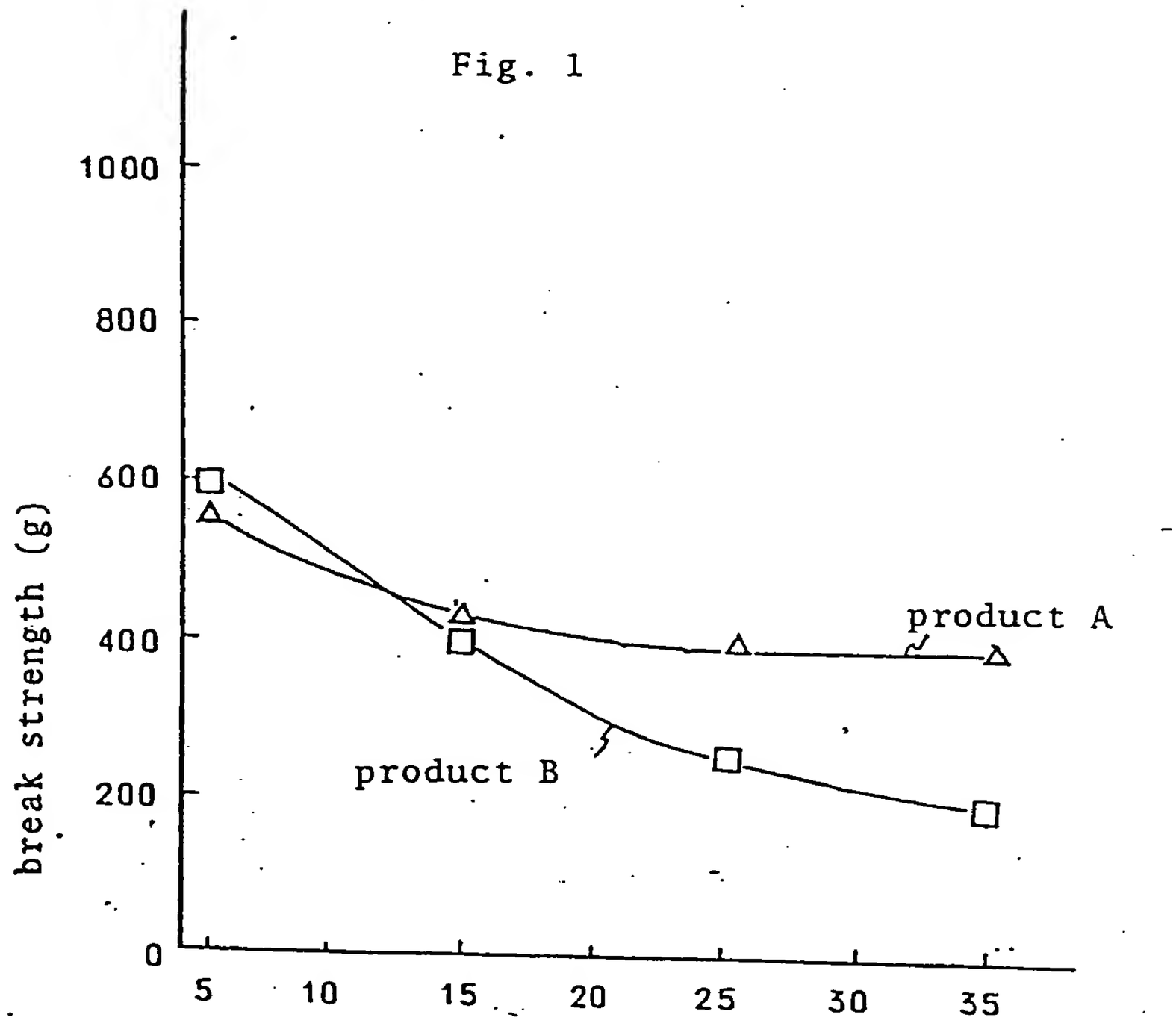
... (I)

in which one of R1, R2 and R3 is a straight-chain fatty acid group havihg 18 to 22 carbon atoms, another is 2-ethylhexanic acid group and the other is hydrogen.

9. A glyceride mixture obtained by the process as defined in Claim 1, in which the diglyceride has formula (I) in which one of R1, R2 and R3 is a branched, saturated fatty acid group selected from the group consisting of:

(a) methyl-isostearic acid group having the formula:

Fig. 1


1000
800
600
400
200
0
break strength (g)
product A
product B
5
10
15
20
25
30
35
temperature °C